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THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

David R. Battiste

Serial No.: 09/705,316

Filed: November 3, 2000

For: IMPROVED MONITORING AND
CONTROL OF PROCESSES FOR
MAKING 1-HEXENE

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Group Art Unit: 1764

Examiner: Buttner, David J.

Atty. Docket: CPCM:0008/FLE
33938US00

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April 17, 2006
Date

Betty L. Broyles
Betty L. Broyles

Sir:

APPEAL BRIEF PURSUANT TO 37 C.F.R. §§ 41.31 AND 41.37

This Appeal Brief is being filed in furtherance to the Notice of Appeal mailed on December 29, 2005, and received by the Patent Office on January 17, 2006. Appellant respectfully requests that the Commissioner charge the requisite fee of \$500.00 for the Appeal Brief to the credit card listed on the attached PTO-2038.

Appellant hereby requests a one-month extension in the statutory period from March 17, 2006 to April 17, 2005 in accordance with 37 C.F.R. § 1.136. The Commissioner is authorized to charge the requisite fee of \$120.00 for a one-month extension of time to the credit card listed on the attached PTO-2038.

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The Commissioner is authorized to charge any additional fees which may be required, to the credit card listed on the attached PTO-2038. Further, if the PTO-2038 is missing, if the amount listed thereon is insufficient, or if the amount is unable to be charged to the credit card for any other reason, the Commissioner is authorized to charge Deposit Account No. 06-1315; Order No. CPCM:0008/FLE (33938US00).

1. **REAL PARTY IN INTEREST**

The real party in interest is Chevron Phillips Chemical Company LP, the Assignee of the above-referenced application by virtue of the executed Assignment, which will be directly affected by the Board's decision in the pending appeal.

2. **RELATED APPEALS AND INTERFERENCES**

Appellant is unaware of any other appeals or interferences related to this Appeal. The undersigned is Appellant's legal representative in this Appeal.

3. **STATUS OF CLAIMS**

Claims 1-5, 8-12, 30-33, and 35-37 are currently under final rejection and, thus, are the subject of this appeal.

4. **STATUS OF AMENDMENTS**

An amendment subsequent to the Final Office Action mailed on September 29, 2005 was submitted by Appellant to cancel claims 13-21, 38, and 39. *See* Response to Final Office Action, page 7. The Examiner entered this amendment. *See* Advisory

Action mailed December 21, 2005. No other amendments have been submitted or entered subsequent to the Final Office Action mailed on September 29, 2005.

5. **SUMMARY OF CLAIMED SUBJECT MATTER**

The present application contains two independent claims, namely, claims 1 and 30, both of which have been improperly rejected and, thus, are subject to this Appeal. The subject matter of these two independent claims is summarized below.

An embodiment of claim 1 generally provides for a process for olefin oligomerization including providing a reaction mixture to a reactor, the reaction mixture having at least a reactant olefin monomer (e.g., ethylene) and a catalyst system suitable for the oligomerization of olefin monomers (e.g., 1-hexene). *See, e.g.*, Application, page 12, lines 5-25. The process further comprises contacting the olefin monomer and the catalyst system in a reaction zone and monitoring an olefin oligomerization reaction by using low-resolution Raman spectrometry equipment to provide an output signal representative of one or more chemical components (e.g., ethylene) of the reaction. *See, e.g.*, Application, page 12, line 25 – page 13, line 31.

An embodiment of claim 30 generally provides for a trimerization process including monitoring a trimerization reaction (e.g., of ethylene) by using Raman spectrometry equipment, wherein the Raman spectrometry equipment comprises low resolution Raman spectrometry equipment (e.g., having a spectral resolution of about 15 cm^{-1}), and recovering 1-hexene from the trimerization reaction. *See, e.g.*, Application,

page 8, lines 10-14; page 9, lines 5-24 (“Spectral resolution for such a spectrometer is about 15 cm^{-1} , which places it in the category of low resolution spectrometry equipment.”).

6. **GROUND OF REJECTIONS TO BE REVIEWED ON APPEAL**

First Ground of Rejection:

Appellant respectfully requests that the Board review and reverse the Examiner’s first ground of rejection, in which claims 1-5, 8-11, 13-21, 30-33, and 35-39 were rejected under 35 U.S.C. § 103(a) as obvious over Lashier et al. (U.S. Patent No. 5,689,028) in view of Alsmeyer et al. (U.S. Patent No. 5,638,172).

Second Ground of Rejection:

Appellant respectfully requests that the Board review and reverse the Examiner’s second ground of rejection, in which claims 12 and 37 were rejected under 35 U.S.C. § 103(a) as being unpatentable over Lashier et al. and Alsmeyer et al. in further view of Tanaka et al. (U.S. Patent No. 5,750,817).

7. **ARGUMENT**

As discussed in detail below, the Examiner has improperly rejected the pending claims. Further, the Examiner has misapplied long-standing and binding legal precedents and principles in rejecting the claims under 35 U.S.C. § 103(a). Accordingly, Appellant

respectfully requests full and favorable consideration by the Board, as Appellant strongly believes that claims 1-5, 8-12, 30-33, and 35-37 are currently in condition for allowance.

First Ground of Rejection

The Examiner rejected claims 1-5, 8-11, 13-21, 30-33, and 35-39 under 35 U.S.C. § 103(a) as obvious over Lashier et al. (U.S. Patent No. 5,689,028) in view of Alsmeyer et al. (U.S. Patent No. 5,638,172). Appellant respectfully traverses this rejection.

Legal Precedent

The burden of establishing a *prima facie* case of obviousness falls on the Examiner. *Ex parte Wolters and Kuypers*, 214 U.S.P.Q. 735 (PTO Bd. App. 1979). To establish a *prima facie* case, the Examiner must show that the modified reference includes *all* of the claimed elements, and provide a convincing line of reason as to why one of ordinary skill in the art would have found the claimed invention to have been obvious in light of the teaching of the reference. *See Ex parte Clapp*, 227 U.S.P.Q. 972 (B.P.A.I. 1985). One cannot use hindsight reconstruction to deprecate the claimed invention. *In re Fine*, 837 F.2d 1071, 5 U.S.P.Q.2d 1596 (Fed. Cir. 1988).

Deficiencies of the Rejection

The Examiner's rejection is insufficient for at least three reasons. First, the cited combination fails to teach all of the features recited in the independent claims. For example, as acknowledged by the Examiner, Lashier fails to disclose the use of Raman

spectroscopy, and the Alsmeyer reference (relied upon to teach the use of Raman spectrometry equipment) does *not* disclose the *resolution* of the Raman equipment or the use of Raman spectroscopy in controlling an olefin oligomerization reaction. *See, e.g.*, Office Action Mailed April 11, 2005, page 4. Second, there is no motivation to modify the Lashier system to incorporate use of Raman spectroscopy, much less to incorporate *low-resolution* Raman spectroscopy. Third, the Examiner impermissibly used hindsight in combining the references as alleged.

Moreover, the Examiner's implicit assertion that the sole difference between the uses of high and low resolution Raman spectroscopy is the selection of "appropriate wavelengths" is not supported by any evidence. The resolution of a Raman spectrometer, which refers to the ability to resolve spectral features, is a pertinent, important, and non-trivial aspect of the device, as taught in the art, as presently disclosed, and as presently claimed.

1. Features of Claims 1 and 30 are Missing from the Cited Combination

Independent claim 1 recites "monitoring an *olefin oligomerization* reaction by using *low-resolution* Raman spectrometry equipment." (Emphasis added). Independent claim 30 recites "monitoring a *trimerization reaction* by using Raman spectrometry equipment, wherein the Raman spectrometry equipment comprises *low resolution* Raman spectrometry equipment." (Emphasis added).

The Examiner has not shown that the Alsmeyer device falls within the category of a *low-resolution device*. See, e.g., Application, page 9, lines 23-24. Therefore, the Examiner has not met his burden in demonstrating that the cited combination includes all of the claimed elements. Accordingly, the Examiner has failed to establish a *prima facie* case of obviousness with regard to independent claims 1 and 30, and their dependent claims.

In formulating the rejection, the Examiner stated that it would have been obvious to use the “appropriate wave lengths” to monitor the Lashier process. See Final Office Action, page 4. However, the Examiner misses the point. The selection of “appropriate wave lengths” is irrelevant to the question of whether Alsmeyer discloses a low-resolution device.

Any given Raman device possesses a certain resolution capability, placing that device in either the category of a low resolution device or a high resolution device. See, e.g., Application, page 9, lines 23-24 (disclosing that a Raman device having a resolution capability of 15 cm^{-1} falls in the category of a low resolution device). Appellant believes it is well known in the art that a resolution capability generally greater than 8 cm^{-1} places the Raman device in the category of a low resolution device. See, e.g., http://www.avaloninst.com/content/raman_information/glossary.htm (last accessed, March 17, 2006); see also <http://www.enwaveopt.com/doc/SpectroscopyArticle.pdf>

(explaining that high resolution Raman is a resolution less than 6 cm^{-1}) (copy of article provided herewith).

Appellant emphasizes that it is the Examiner's burden, not Appellant's, to show that the Alsmeyer device is a low-resolution device. Again, the Examiner has failed to meet this burden and therefore has not established a *prima facie* case of obviousness.

2. *No Reason to Modify Lashier as Suggested by the Examiner*

The Examiner proposed to modify the Lashier 1-hexene process to incorporate the Alsmeyer Raman device to monitor the (trimerization) conversion of ethylene to 1-hexene. *See, e.g.*, Final Office Action, page 4. However, the peaks of the trimerization to measure to determine conversion are ethylene and 1-hexene at 1620 cm^{-1} and 1640 cm^{-1} , respectively. *See, e.g.*, Response to Office Action Mailed April 11, 2005; Application page 4 lines, 3-12. Therefore, since the peaks are so close, one of ordinary skill in the art, without the benefit of the Appellant's disclosure, would dismiss the use of low-resolution Raman spectrometry to measure conversion in the monitoring and control of the Lashier ethylene trimerization process.

Not only has the Examiner failed to show that the Alsmeyer reference discloses a low-resolution instrument as claimed, the Examiner has not shown nor explained how the Alsmeyer reference teaches the applicability of or the ability to use a low-resolution

Raman device in the Lashier process or in the claimed processes. Appellant respectfully submits that the Examiner has failed to establish a *prima facie* case of obviousness.

3. *Improper Combination – Impermissible Hindsight*

Apparently, the Examiner believes that because Alsmeyer discloses the use of Raman spectroscopy in a polyester process, the Alsmeyer reference can be paired with any other reference disclosing a different process to render the use of Raman spectroscopy in that different process as obvious. *See* Final Office Action, pages 3-4 (suggesting that use of Raman in Lashier is obvious because “Alsmeyer discloses that the Raman spectrometry has a lots [sic] of advantages for monitoring chemical processes.”). However, Appellant respectfully asserts that the Examiner had no reason to even consider the use of Raman spectroscopy in the Lashier 1-hexene process, other than impermissible hindsight based on Appellant’s disclosure. The Federal Circuit has warned that the Examiner must not “fall victim to the insidious effect of a hindsight syndrome wherein that which only the inventor taught is used against its teacher.” *See In re Dembiczak* 50 U.S.P.Q. 2d 52 (Fed. Cir.1999) (quoting *W.L. Gore & Assoc., Inc. v. Garlock, Inc.*, 220 U.S.P.Q. 303, 313 (Fed. Cir.1983)); *see also In re Fine*, 837 F.2d 1071, 5 U.S.P.Q.2d 1596 (Fed. Cir. 1988) (explaining that one cannot use hindsight reconstruction to pick and choose among isolated disclosures in the prior art to deprecate the claimed invention).

Clearly, without the benefit of Appellant's disclosure, the Examiner (or one of ordinary skill in the art) would *not* know or think it feasible to employ a Raman device, let alone a low resolution Raman device, in the 1-hexene process of Lashier. After all, as discussed below, the Alsmeyer polyester process (a condensation reaction) and the Lashier 1-hexene process (an addition reaction) utilize disparate chemical reactions.

With regard to the specific proposal by the Examiner to measure *conversion* in Lashier with the Alsmeyer Raman, the application of Raman is much easier in the Alsmeyer process than in the Lashier process. The Alsmeyer polymerization reactants and product polymer polyester are dissimilar compounds having dissimilar functional groups that have dissimilar Raman wavelengths, and therefore are relatively straightforward to differentiate and measure, especially with the high resolution Raman spectrometer apparently taught by Alsmeyer. Conversely, in Lashier, the key structural feature of the reactant ethylene and product 1-hexene, the carbon-carbon double bond, has similar wavelengths which make them inherently more difficult to differentiate and measure with Raman spectroscopy, especially by a low resolution Raman spectrometer, as claimed. *See, e.g.*, Application, page 14, lines 3-33.

The present application recognizes the difficulty of differentiating ethylene and 1-hexene with low-resolution Raman, stating:

In such cases [with ethylene and 1-hexene], obtaining a calibration model that can distinguish and correct [sic] quantify these components may seem impossible. It has been observed that such a calibration model is obtainable,

though with more difficulty than where the components have peaks that are separate and readily distinguishable. Furthermore, it has been discovered that such a calibration model may be obtained and used even with low resolution Raman spectrometry equipment.

Application, page 15, lines 1-10.

Clearly, the cited combination proposed by the Examiner does not inform one of ordinary skill in the art in the use of *low-resolution* Raman spectroscopy in a *1-hexene process or similar oligomerization process*. Alsmeyer does not teach the capability of differentiating between the Raman peaks of ethylene and 1-hexene, as discussed above. See Application, page 4 lines 3-12. Such a modification of either cited reference is clearly not obvious. See Final Office Action, page 4; Application, page 4, lines 3-21; page 18, lines 14-34. Again, Appellant respectfully asserts that the Examiner has employed impermissible hindsight in attempting to modify both the Lashier and Alsmeyer references to read on the present claims. See *In re Fine*, 837 F.2d 1071, 5 U.S.P.Q.2d 1596 (Fed. Cir. 1988).

Additionally, the two processes pose different functional relationships between the monomers and products which impact the ability to measure conversion and to control the respective processes. Alsmeyer's process allows one to measure and control, spectroscopically, at least one monomer which has a functional feature (the hydroxy group of the alcohol monomer) different than the functional feature of the resulting product (the ester group of the resultant polyester). In contrast, Lashier's process must be

able to measure, spectroscopically, the difference between the single monomer (ethylene) and a resultant product (1-hexene), which have the same spectroscopic structural feature, a carbon-carbon double bond.

The Alsmeyer process produces a polymer by creating an ester group (which has a dissimilar functional group than at least one of the Alsmeyer monomers) while Lashier's process produces an oligomer by creating two carbon-carbon single bonds while retaining a carbon-carbon double bond (which is also present in the single and only monomer of Lashier). It should also be noted that the Alsmeyer process utilizes two monomers having two dissimilar functional groups (an alcohol and an ester), whereas Lashier's process utilizes a single monomer (ethylene). Therefore, for this reason as well, the Raman approach is radically different in measuring monomer concentration in Alsmeyer as would be done in Lashier. Such differences between Alsmeyer and Lashier clearly impact the ability/configuration of the Raman device in providing "an output signal representative of one or more chemical components of the reaction," as recited in claim 1. Plainly, the Examiner has employed impermissible hindsight, without any teaching or direction except for that of the present disclosure, to justify the combination of Alsmeyer and Lashier.

In sum, the Examiner has not overcome the hindsight gap to explain why one of ordinary skill in the art of *1-hexene production* (an addition reaction employing a single monomer which is difficult to differentiate from the product 1-hexene with Raman)

would look to a *polyester process* (a condensation reaction employing two monomers which are easy to differentiate from the product polyester with Raman and easy to differentiate between themselves with Raman). To be sure, the demands placed upon the Raman spectrometer in *Alsmeyer's polyester process* are very different than the demands that would be placed upon the Raman spectrometer in the *Lashier 1-hexene process*. Appellant stresses that the Examiner has failed to bridge the enormous gap that must be overcome to find motivation to combine Alsmeyer and Lashier, as proposed by the Examiner.

4. *Selection of Wavelengths*

In the Advisory Action mailed December 21, 2005, the Examiner posited that once the “appropriate wavelengths [are] selected, then the equipment having such a selected wave length would be selected to be used.” This statement implicitly recognizes that it is not the wavelength that can be controlled by the skilled artisan, but the equipment utilized, in terms of resolution (among other parameters), that can be specified by the skilled artisan. Therefore, considering the nearness of the “appropriate wavelengths” for the ethylene to 1-hexene trimerization (as previously discussed), the skilled artisan would not select a low-resolution Raman spectrometer to measure ethylene and 1-hexene within the ethylene trimerization process and would in fact choose a high resolution instrument for controlling the ethylene to 1-hexene trimerization process.

The Examiner demonstrates a misunderstanding of the art in implying that the difference between the use of high and low resolution Raman spectroscopy is merely the selection of appropriate wavelengths. Furthermore, the Examiner has provided no evidence, either in the form of references or knowledge known to one of skill in the art, to support the assertion that the only difference in the application of high resolution Raman spectroscopy is the selection of appropriate wavelengths. To explain, Raman spectrometry measures the wavelengths of scattered radiation obtained by irradiating a sample with a source of visible monochromatic radiation. Regardless of the resolution of the Raman instrument, the scattered radiation will have the same wavelengths.

The resolution of the Raman spectrometer impacts whether or not the instrument can differentiate between two or more peaks of scattered radiation. While, it is true that any particular compound will have multiple wavelengths that can be measured by a Raman spectrometer, not all of these wavelengths may be useful (e.g., for monitoring a process or for measuring a component concentration) due to the overlap of the Raman peaks of other compounds within the process system. Thus, the skilled artisan does not have an infinite number of wavelengths to choose from and may actually be limited to only a few useful wavelengths. For a particular reaction, the useful wavelengths will depend on the reagents and products of the reaction, and it is the resolution of the Raman spectrometer that the skilled artisan can select and control to accommodate the particular demands for monitoring and differentiating the useful wavelengths of any particular chemical process such as an olefin oligomerization process (or trimerization process), as

claimed. Here, the Examiner has not explained the motivation of why one skilled in the art would specify a low-resolution device to monitor the Lashier process. This is especially clear when considering that one of ordinary skill in the art would recognize the difficulties and limitations of utilizing low resolution Raman to monitor an olefin oligomerization process (or trimerization process) which has useful wavelength peaks that are difficult to differentiate using a low resolution Raman spectrometer.

Request Withdrawal of Rejection

In view of the deficiencies of the Lashier and Alsmeyer references discussed above, Appellant respectfully requests that the Board direct the Examiner to withdraw the rejection of claims 1-5, 8-12, 30-33, and 35-37.

Second Ground of Rejection

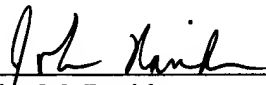
The Examiner rejected dependent claims 12 and 37 under 35 U.S.C. 103(a) as being unpatentable over Lashier in view of Alsmeyer, et al., and further in view of Tanaka et al. (U.S. Patent No. 5,750,817). Appellant respectfully traverses this rejection. The Tanaka reference does not obviate the deficiencies of the Alsmeyer and Lashier references discussed above with regard to the independent claims. Therefore, rejected claims 12 and 37 are believed to be patentable over the cited combination by virtue of their dependency on an allowable base claim and also because of the subject matter they separately recite. Accordingly, Appellant respectfully requests that the Board direct the Examiner to withdraw the rejection of claims 12 and 37 and allow the claims.

CONCLUSION

If the Examiner or the Board believes that a telephonic interview would assist in the prosecution of the present application to allowance, such an interview with the undersigned is sincerely invited.

Respectfully submitted,

Date: April 17, 2006



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8. APPENDIX OF CLAIMS ON APPEAL

1. (previously presented) A process for olefin oligomerization in a reactor,
the process comprising:
providing a reaction mixture in the reactor, the reaction mixture comprising:
at least one reactant comprising at least one olefin monomer and optionally
hydrogen; and
a catalyst system suitable for the oligomerization of olefin monomers;
contacting the olefin monomer and the catalyst system in a reaction zone;
monitoring an olefin oligomerization reaction by using low-resolution
Raman spectrometry equipment to provide an output signal
representative of one or more chemical components of the reaction;
and
recovering an oligomer.
2. (previously presented) The olefin oligomerization process of claim 1,
wherein the output signal is representative of a concentration of one of the reactants or the
oligomer.
3. (previously presented) The olefin oligomerization process of claim 1,
comprising adjusting the olefin oligomerization reaction in response to the output signal
provided by the Raman spectrometry equipment.

4. (previously presented) The olefin oligomerization process of claim 1, wherein the olefin oligomerization reaction is adjusted by adjusting the amount within the reaction mixture of at least one of the reactants, the oligomer or the catalyst system.

5. (previously presented) The olefin oligomerization process of claim 1, wherein the Raman spectrometry equipment is operatively connected to a Raman fiber optic probe that is in contact with the olefin oligomerization reaction or the oligomer.

6. (cancelled).

7. (cancelled).

8. (previously presented) The olefin oligomerization process of claim 1, wherein the low resolution Raman spectrometry equipment has a resolution in the range of from about 15 wavenumbers to about 30 wavenumbers.

9. (previously presented) The olefin oligomerization process of claim 1, wherein the reactants comprise hydrogen.

10. (previously presented) The olefin oligomerization process of claim 1, wherein the oligomerization reaction is a trimerization reaction.

11. (previously presented) The olefin oligomerization process of claim 1, wherein the monomer comprises ethylene and the oligomer comprises 1 – hexene.

12. (previously presented) The olefin oligomerization process of claim 1, wherein the process is performed in two or more reactors connected in series, wherein effluent from an upstream reactor is provided as input to a downstream reactor, wherein the monitoring comprises determining a concentration of the monomer in the effluent by the Raman spectrometry equipment, and comprising adjusting an amount of monomer or comonomer fed to the downstream reactor.

13-29. (cancelled).

30. (previously presented) A trimerization process, the process comprising:
monitoring a trimerization reaction by using Raman spectrometry equipment,
wherein the Raman spectrometry equipment comprises low resolution
Raman spectrometry equipment; and
recovering 1-hexene from the trimerization reaction.

31. (previously presented) The trimerization process of claim 30, comprising adjusting a condition of the trimerization reaction in response to an output signal provided by the Raman spectrometry equipment.

32. (previously presented) The trimerization process of claim 31, wherein adjusting the trimerization reaction condition comprises adjusting an amount of an ethylene monomer, a catalyst system, or the 1-hexene, or any combination thereof, in response to the output signal.

33. (previously presented) The trimerization process of claim 30, wherein the Raman spectrometry equipment comprises a Raman fiber optic probe adapted to contact the trimerization reaction.

34. (cancelled).

35. (previously presented) The trimerization process of claim 30, wherein the low resolution Raman spectrometry equipment has a resolution in the range of from about 15 wavenumbers to about 30 wavenumbers.

36. (previously presented) The trimerization process of claim 30, wherein the trimerization reaction comprises ethylene monomer, a catalyst system, and hydrogen.

37. (previously presented) The trimerization process of claim 30, wherein the process is performed in two or more reactors connected in series, wherein effluent from an upstream reactor is provided as input to a downstream reactor, wherein the monitoring comprises determining a concentration of an ethylene monomer in the effluent by the

Raman spectrometry equipment, and comprising providing an amount of the ethylene monomer in addition to the effluent to the downstream reactor in response to the determined concentration of the ethylene monomer in the effluent.

38. (cancelled).

39. (cancelled).

9. APPENDIX OF EVIDENCE

See the attached article entitled “A New Era in Affordable Raman Spectroscopy.”

10. APPENDIX OF RELATED PROCEEDINGS

None.

A New Era in Affordable Raman Spectroscopy

This article overviews several recent advancements in Raman components that are enabling high analytical performance in low-cost Raman instruments.

Tony Lam

Raman spectroscopy is an ideal tool for chemical analysis due to its unique advantages over other analytical techniques. It is a nondestructive and noncontacting method of obtaining the fingerprint spectrum of materials, requiring no special sample preparation. Raman can analyze samples via sample plastic bags, glass vials, and in aqueous solution. It does not require a large amount of a sample to do analysis; the sample can be as small as 1–2 µm across. A short amount of measuring time, normally a few seconds, is required to obtain a Raman spectrum. Thus, it can be used to monitor chemical reactions in real time.

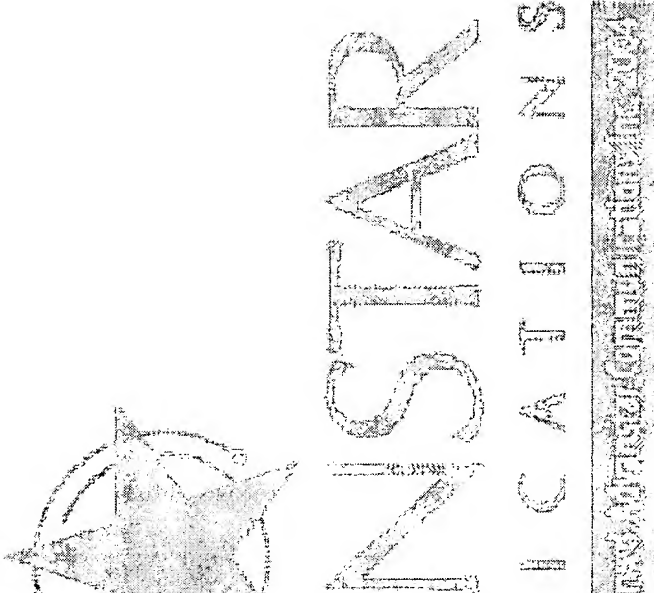
Despite the fact that Raman spectroscopy has so many advantages, it still is not in widespread use. The main reason is the high cost typically associated with Raman analyzer systems. Currently, a high-resolution and high signal-to-noise ratio Raman analyzer can be priced from \$40,000 and above. On the other hand, there is a market need for low-cost Raman analyzer systems as general laboratory tools. However, those systems usually are

equipped with low-resolution, low-power visible lasers, and low signal-to-noise ratios, which is not adequate enough to perform any high performance chemical analysis. Therefore, better-resolution and lower-cost Raman systems are key to increasing and enabling greater acceptance and usage of Raman spectroscopy.

This article presents a few key advancements in Raman components that will enable low costs and high performance. It also establishes the figure of merit to identify and characterize Raman systems in terms of high resolution and low cost. Finally, Raman applications and sample Raman spectra in pharmaceutical, petrochemical processing, and plastic recycling applications will be presented.

Modern Raman Systems

A typical laboratory Raman analyzer system consists of four major components: the excitation source, the collection device, the spectrograph, and the post-processing software. The excitation source must be strong enough to generate sufficient Raman signals, and



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Raman Components

monochromatic light to provide clean and uncomplicated spectra. A laser typically is used as the excitation source because it can provide a coherent beam of monochromatic light with high intensity. The collection device is the fiber-optic probe. It collects the scattered photons, filters out the Rayleigh scattering, and sends the Raman signals to the spectrograph. The spectrograph then separates the Raman signals by their wavelengths and transfers them to the light detector, which records the intensity of the accumulated photons at its own wavelength. These recorded data then are passed to the postprocessing software to display as a Raman spectrum.

Several types of lasers can be used as the excitation source for Raman spectroscopy. They are Ar⁺ ion (488.0 and 514.5 nm), Kr⁺ ion (530.9 and 647.1 nm), HeNe (632.8 nm), Nd:YAG (1064 nm), and diode (630 and 980 nm) lasers (1). Due to recent advancements in diode laser technology, it is the best candidate to be utilized in low-cost, portable Raman analyzer systems because of its relatively low cost, compact size, high reliability (>10,000-h lifetime), and near-infrared (NIR) emission wavelength for fluorescence reduction. A typical diode laser used in a modern Raman analyzer system is a high power laser diode (>300 mW), with wavelengths ranging from 630 to 980 nm.

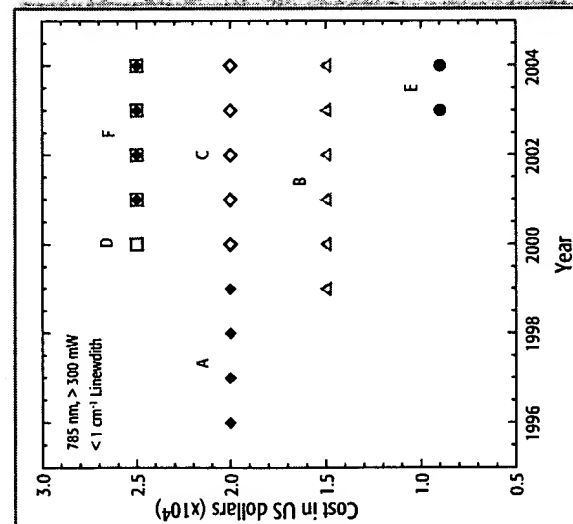


Figure 1. Cost survey of diode-based Raman spectroscopy lasers (A, B, C, D, E, and F are different Raman spectroscopy laser manufacturers).

Recent developments in diode laser wavelength stabilization and linewidth narrowing have been very dramatic. Current wavelength stabilization designs include Littrow with traditional gratings, Littmann with traditional gratings, fiber Bragg gratings, volume Bragg gratings, distributed feedback lasers (DFBs), distributed Bragg reflector lasers (DBRs), and master oscillator power amplifier lasers (MOPAs). Some designs also integrate a bandpass filter or amplified spontaneous emission (ASE) reduction technique to remove the unwanted ASE interference that often is seen in a high-power diode laser. All these lasers should

at least provide 150 mW in optical power, a stabilized center wavelength within a tenth of a wavenumber, and a spectral linewidth of less than 1 cm⁻¹ for a high-resolution Raman system. A laser linewidth (~3–4 cm⁻¹) close to the spectrometer's resolution is not ideal because the system's overall spectral profile or response will be the convolution of the two responses (laser linewidth and spectrometer's resolution). Thus, any laser spectral profile changes due to temperature, current, or any other nonlinearities will affect the overall system spectral profile and cause inaccuracies in chemometric prediction. Figure 1 depicts a cost survey over the past eight years for wavelength-stabilized, 785-nm, 300-mW, 1-cm⁻¹ linewidth Raman spectroscopy laser systems on the market.

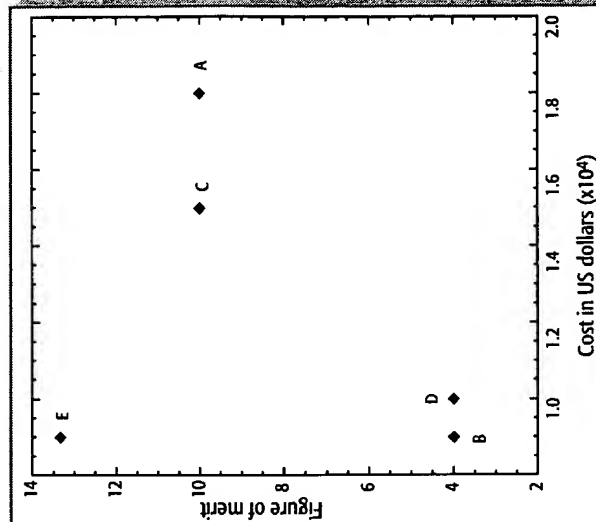


Figure 2. Comparison of diode-based Raman laser sources on the current market (figure of merit = power/linewidth).

Due to the recent development of a silicon CCD camera, the CCD sensor has replaced the single channel detector, photomultiplier tube (PMT) and avalanche photodiodes (APD), as a multichannel photon detector in the spectrograph. It can detect radiation from 400 to 1100 nm (2). In addition, the CCD sensor will reduce integration time because it allows spectrum multiplexing. A typical integration time of the CCD spectrograph is less than 30 s.

A general laboratory Raman probe is composed of two fibers. The excitation fiber is used to deliver the excitation source to a sample. The collection fiber is used to collect Raman signals and deliver it to the spectrograph. Normally, the bandpass filter and band-reject filter are integrated into

Raman Components

the fiber-optic probe head to remove the laser Rayleigh scattering, silica Raman interference from the fiber, and ASE from the laser excitation source.

The data collected from the spectrograph then are sent to the software. The software then converts the data into the Raman spectrum and displays it on an x-y chart. The x axis of the chart is the wavenumber, while the y axis is the intensity of the spectrum.

Resolution of Raman Systems

Three basic bandpass filters are used in a typical Raman measuring system to determine the overall Raman spectrum quality (that is, resolution).

These three bandpass filters are: laser line-width bandpass, spectrometer bandpass, and sample bandpass (natural line-width) filters.

Ideally, a laser line-width bandpass filter should be much less than the spectrometer bandpass filter. In this case, the spectrometer will be the only factor in determining the Raman system's bandpass filter. If the bandpass filters of the two (that is, laser and spectrometer) are close, the system's bandpass filter will be a convolutional bandpass filter of the two components. Generally, a spectrometer bandpass filter's profile is much more stable than the laser bandpass filter profile, thus a much narrower laser line-width bandpass filter is preferred and could make a system much more stable.

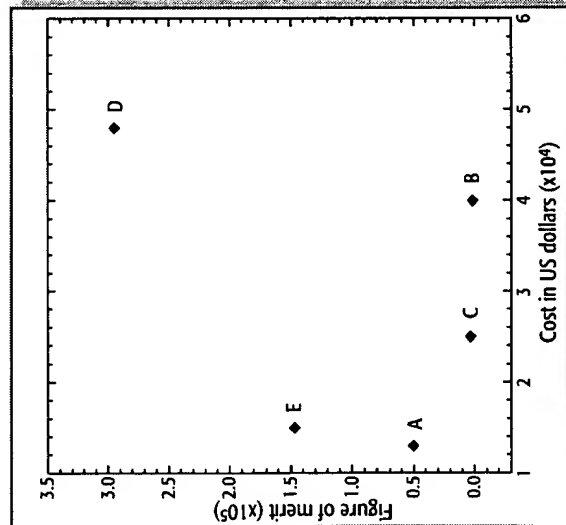


Figure 3. Comparison of laboratory Raman systems on the current market (figure of merit = [coverage x power]/[resolution]).

For most Raman applications in solid and liquid samples, a system resolution of 6 cm⁻¹ or less is sufficient. Unfortunately, any high-resolution (<6 cm⁻¹) Raman system usually is highly priced primarily because of the high cost of the high power (>300 mW), wavelength-stabilized, and line-width narrowed (<1 cm⁻¹) Raman spectroscopy laser.

Costs of Raman Systems

To compare the cost of different Raman systems currently on the market, a figure of merit is adopted as a way to normalize different features and performances for a fair comparison. The higher the figure of merit, the better the system's performance. This section of the article compares the costs of the laser sources and the overall Raman systems. The cost

of laser sources is compared because the laser still is the major cost component for a Raman system. The figure of merit of the laser is defined as the laser power inversely proportional with the laser line-width:

$$\text{Figure of merit} = \frac{\text{power}}{\text{linewidth}} [1]$$

Using Equation 1, the figures of merit of lasers (A-E) are calculated and mapped in Figure 2.

Observing the figure-of-merit chart (Figure 2), the laser excitation sources are divided into three groups. One group is the high performance and high cost

group, including A and C laser sources. The second group is the low-performance and low-cost group, including B and D laser sources. The last group, E laser sources, is the high performance and low cost group.

The figure-of-merit of the Raman system is defined as the product of the spectral range (coverage) and the laser power divided by the system resolution:

$$\text{Figure of merit} = \frac{(\text{coverage} \times \text{power})}{(\text{resolution})} [2]$$

Using Equation 2, the figures of merit of Raman systems (A-E) are calculated and mapped in Figure 3.

Observing the figure-of-merit chart of the Raman system (Figure 3), the A and E Raman systems are considered to be the medium-performance and low-cost systems. The B and C systems are considered to be low-performance and high-cost systems. The D system is considered a high-end system, high performance versus high cost. It is the

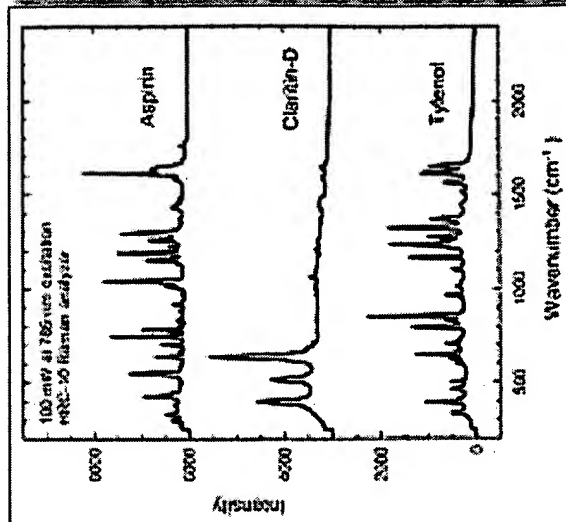


Figure 4. Raman spectra of OTC medicines.

Raman spectroscopy applications that determine which Raman systems should be used, but for most of the applications, a Raman system that has a 6-cm⁻¹ spectral resolution is sufficient (1).

Applications of Affordable Raman Systems

With high-resolution and low-cost Raman systems, many Raman spectroscopy applications in chemical analysis become feasible. To name a few, Raman spectroscopy is useful in drug identification for the pharmaceutical industry, the control of octane level in gasoline, and the classification of plastic in the plastic recycling industry. To

demonstrate the feasibility of using a low-cost Raman instrument in these applications, the HRC-10 Raman analyzer with less than 6-cm⁻¹ system resolution, manufactured by EnWave Optronics, was chosen to collect Raman

spectra of some over-the-counter medicines, unleaded isooctane levels of Chevron gasoline, and some plastic samples.

Pharmaceutical. One of the advantages of the Raman system is its ability to measure down to 50 cm^{-1} in spectral range compared to the mid-IR system that can only reach approximately 400 cm^{-1} . The feature is very attractive to the pharmaceutical industry because most of the spectra of drug lattices are below 200 cm^{-1} (3). Raman spectroscopy finds its application in lattice vibration study for the characterization of the solid state of a drug and especially for the investigation of polymorphism and amorphous systems. In addition, it finds application in analysis and quantification of drug blends, and in the examination of drug formulations and drug excipient incompatibilities.

Petrochemical. The gasoline purchased from any local gas station has the methyl-*tert*-butyl ether (MTBE) (4) content added to improve the octane number. The octane number is an experimentally determined property of petroleum fuel that defines the quality of engine antiknocking. Raman spectroscopy can be used to identify the octane level within gasoline. An example of the octane level in Chevron unleaded gasoline is shown in Figure 5. Also, Raman systems can be used to measure oxygenate material in the gasoline. According to the U.S.

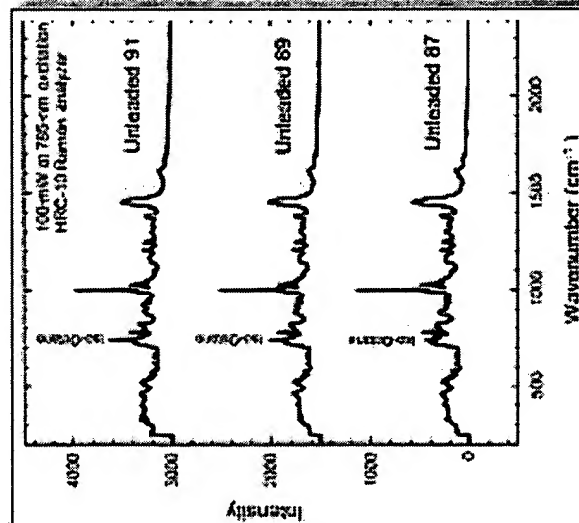


Figure 5. Raman spectra of Chevron unleaded gasoline with various isooctane levels.

lene (PP, 5); polystyrene (PS, 6); and "other," labeled as 7 (5). In the plastics industry, Raman spectroscopy systems find application in real-time monitoring of polymerization reactions to control the processing time, in quantitative compositional analysis of polymer melt streams, and in plastic identification for recycling purposes. Figure 6 shows an example of plastic Raman spectra.

Conclusion

With the current advancements in diode laser technology, Raman systems have been improved on two fronts:

cost and resolution. Raman excitation sources now can be made with a lower cost. In addition, laser wavelength stabilizing and linewidth narrowing have improved the resolution of Raman systems. Consequently, these advancements have eliminated the high costs associated with the high-resolution system and brought this novel technology to every corner of life. It signifies a new era in Raman spectroscopy. Perhaps, within five years, it will find itself within many potential applications that have not been considered previously for chemical analysis.

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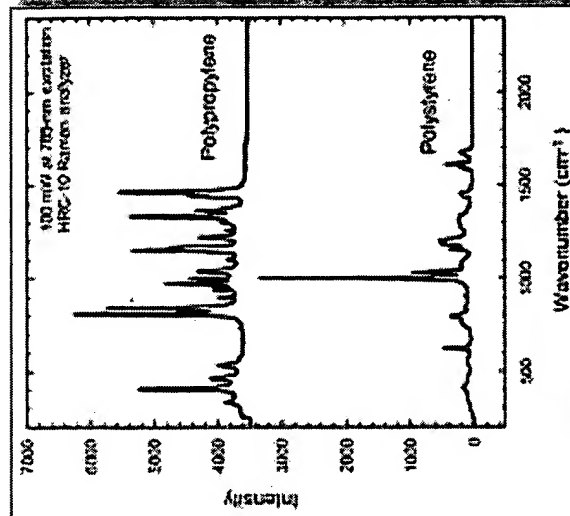


Figure 6. Raman spectra of polypropylene and polystyrene plastics.

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